PATENT SPECIFICATION

DRAWINGS ATTACHED

906,440

Date of Application and filing Complete Specification Feb. 8, 1960.
No. 4382/60.
Application made in France (No. 783402) on March 4, 1959.
Complete Specification Published Sept. 19, 1962.

The inventor of this invention in the sense of being the actual deviser thereof within the meaning of Section 16 of the Patents Act, 1949 is Alexandre Jules Jacques Maurin, a French Citizen of 16 rue de Varize, Paris, France.

Index at acceptance: —Class 41, A2(B1:C2:D:X1), A9, B8.
International Classification:—B01k.

COMPLETE SPECIFICATION

Electrolytic Process for the Treatment of Sea Water

We, COMPAGNIE DE CONSTRUCTION DE GROS MATERIEL ELECTRO MECANIQUE, a

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SPECIFICATION NO. 906,440

By a direction given under Section 17(1) of the Patents Act 1949 this application proceeded in the name of Compagnie Electro-Mecanique, a French Body Corporate, of 12, Rue Portalis, Paris 8e, France.

THE PATENT OFFICE

DS 71614/1(3)/R.109 200 2/63 PI

It has already been proposed that sea water or brackish water should be subjected to an electrolytic softening treatment. Thus Specification No. 823,531 describes a process in which sea water is electrolysed upstream of the apparatus in which it is used, by means of one or more cells provided with metallic electrodes with the object of rendering said water alkaline. The cell used in the process of said specification may comprise a porous partition or diaphragm between the electrodes to separate, at least partially, the liquid (anolyte) which contains, in solution, the products formed by the anodic reactions and the liquid (catholyte) which contains the products formed by the cathodic reactions, and means may be provided for evacuating either the anolyte or the catholyte depending on the circumstances (temperature initial pH and salinity) and the nature of the metal walls to be protected.

We have now found, contrary to the teaching of said specification, that in order to reduce or substantially eliminate the tendency of sea water or of brackish water to form deposits of scale on metallic surfaces, it is preferable to render said water slightly acid and more particularly to create, at least tem-

[*Price* 4*s*. 6*d*.]

the rates of flow of the respective effluents before mixing as a function of the pH measured after mixing.

It is also possible to feed the anodic compartment of the cell having a metallic anode with the anodic effluent of the other and, in this case, to regulate both the rate of flow of this effluent and the rate of supply to the cathodic compartment of the cell having a metallic anode as a function of the pH of the anodic effluent of the latter cell.

In order that the invention may be more fully understood, two embodiments thereof will now be described, by way of example, with reference to the accompanying drawing, in which:—

Figure 1 shows diagrammatically a first means of carrying out the invention according to which the two electrolytic cells are fed in parallel;

Figure 2 shows diagrammatically a second means of carrying out the invention according to which said two cells are fed in series; and

Figure 3 shows a constructional detail of the cells.

According to Figure 1, two electrolytic cells I and II receive sea water to be treated

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COMPLETE SPECIFICATION

Electrolytic Process for the Treatment of Sea Water

We, COMPAGNIE DE CONSTRUCTION DE GROS MATERIEL ELECTRO MECANIQUE, a French Body Corporate of 37, rue du Rocher, Paris, France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

The present invention relates to an electrolytic process for treating sea water, brackish water or partially softened water with a view to decreasing or removing the tendency of such water to scale metallic surfaces with which it comes into contact, particularly those of pipes and apparatus such as boilers, evaporators and condensers.

It has already been proposed that sea water or brackish water should be subjected to an electrolytic softening treatment. Thus Specification No. 823,531 describes a process in which sea water is electrolysed upstream of the apparatus in which it is used, by means of one or more cells provided with metallic electrodes with the object of rendering said water alkaline. The cell used in the process of said specification may comprise a porous partition or diaphragm between the electrodes to separate, at least partially, the liquid (anolyte) which contains, in solution, the products formed by the anodic reactions and the liquid (catholyte) which contains the products formed by the cathodic reactions, and means may be provided for evacuating either the anolyte or the catholyte depending on the circumstances (temperature initial pH and salinity) and the nature of the metal walls to be protected.

We have now found, contrary to the teaching of said specification, that in order to reduce or substantially eliminate the tendency of sea water or of brackish water to form deposits of scale on metallic surfaces, it is preferable to render said water slightly acid and more particularly to create, at least temporarily, a partially carbonic acidity therein.

According to one feature of the invention, the water to be treated is caused to pass continuously through two diaphragm-type electrolytic cells, one of which comprises an anode of amorphous carbon and the other a metallic anode, particularly an anode essentially composed of iron, the anodic effluents are collected exclusively and the respective rates of flow of these effluents and/or of the liquid passing through the two cells is regulated in such a manner that the pH of the mixed anodic effluents is maintained within the range 4 to 6.4, preferably in the vicinity of 5.2.

It is possible to feed the two cells in parallel, mix the anodic effluents and regulate the rates of flow of the respective effluents before mixing as a function of the pH measured after mixing.

It is also possible to feed the anodic compartment of the cell having a metallic anode with the anodic effluent of the other and, in this case, to regulate both the rate of flow of this effluent and the rate of supply to the cathodic compartment of the cell having a metallic anode as a function of the pH of the anodic effluent of the latter cell.

In order that the invention may be more fully understood, two embodiments thereof will now be described, by way of example, with reference to the accompanying drawing, in which:—

Figure 1 shows diagrammatically a first means of carrying out the invention according to which the two electrolytic cells are fed in parallel;

Figure 2 shows diagrammatically a second means of carrying out the invention according to which said two cells are fed in series; and

Figure 3 shows a constructional detail of the cells.

According to Figure 1, two electrolytic cells I and II receive sea water to be treated

from a main pipeline 3 which feeds them in parallel by means of the respective Y (or three-way) pipes 1 and 2. The first cell I comprises an anode 1*a* of amorphous carbon and a cathode 1*c* of iron or an iron alloy; these two electrodes and the liquids (anolyte and catholyte) in which they are immersed are separated by a porous partition or diaphragm 1*d*; the catholyte is evacuated through a pipe 1*e* while the anolyte alone is transmitted, by means of an adjustable valve 5, to a pipe 4 which feeds the apparatus to be protected from scaling. The anolyte of this cell is acid and contains, in particular, as products of anodic reactions, carbon dioxide (20 to 25 cc. per litre at ordinary temperature and for a final pH of 5.4), hydrochloric acid and hypochlorous acid, these latter products being present in small quantities. The carbon dioxide is presumably produced by the reaction of nascent oxygen, generated by the electrolysis, with the amorphous carbon of the anode; the latter is indeed gradually consumed during operation of the process.

The second cell II comprises electrodes 2*a* and 2*c* both made of iron or of an iron alloy, which are separated, as are the liquids (anolyte and catholyte) in which they are immersed, by a porous partition or diaphragm 2*d*; the catholyte is evacuated through a pipe 2*e* while the anolyte alone is transmitted to the pipe 4 by means of an adjustable valve 6. The anolyte of this cell is acid but less so than that of the cell I (for the same intensity of the electrolysis current); as anodic reaction products it contains, in particular, hydrochloric acid, hypochlorous acid, iron chlorides and oxides, these later being in high concentrations and being formed, it is believed, by reaction of nascent oxygen with the iron of the anode.

The liquids coming from these two cells are mixed in the pipe 4, their relative proportions being regulated by the respective deliveries of the valves 5 and 6, in such a manner that the pH of the water in the pipe 4 is comprised between 4 and 6.4 preferably between 4 and 6; a value of about 5.2 is recommended.

The regulation may be effected, in particular, by means of a device which is sensitive to the pH of the liquid passing through the pipe 4. This device, shown diagrammatically at 7, comprises a pH-meter which supplies an electromotive force, the sense of which depends on the acidity of alkalinity of the liquid and the magnitude of which depends on the modulus (7—pH) or (pH—7) as the case may be, in combination with an amplifier, the output-stage current of which passes in one direction or the other (after possible rectification) through one of the windings of an electric motor 8 provided with two induction windings and the shaft of which is coupled to a mechanism 9 acting in the inverse sense on the position of the valves 5 and 6.

The regulating device thus outlined may, of course, be replaced by any equivalent regulating device.

According to Figure 2, the first electrolytic cell I receives the water to be treated from a pipeline 3 by means of the Y pipe 1, exactly as in the arrangement of Figure 1. Moreover, this cell is similar to that in Figure 1 and its catholyte is evacuated in the same manner through the pipe 1*e*. Its anodic effluent, as distinct from Figure 1, is supplied to the second cell II through a pipe 10 provided with an adjustable valve 11 and there undergoes a second electrolytic treatment. The cell II is similar to the corresponding cell in Figure 1 and, in particular, its cathodic effluent is evacuated through the pipe 2*e*. The anodic effluent of the cell II, which is in series with the former, is alone conveyed through the pipe 4 to the apparatus which it is desired to feed with treated water. Nevertheless, untreated water may likewise be introduced into said cell II by means of the main pipeline 3 and a pipe 12 provided with an adjustable valve 13. The pH of the liquid which passes through the pipe 4 is measured by the pH-meter of a device 7 similar to that in Figure 1 and it can be maintained at a substantially constant value or within the restricted range specified above by the automatic regulation of the positions of the valves 11 and 13 by the members 8 and 9 already mentioned; the member 9 is likewise adapted to regulate, by any known means, the electrolytic current of the cell II, and the valve 13 may be regulated in an independent manner, particularly by hand.

The sections of the pipes and the settings of the various valves are determined in such a manner that, bearing in mind the consumption of treated water by the consumer apparatus, the amount of water which circulates in the anodic and cathodic compartments of the two cells is sufficient to permit the formation, by electrolysis, of the products mentioned above, in the quantities necessary to maintain the pH of the treated water approximately at the required value.

It is essential to note that in the process described in the above-mentioned specification, the treated liquid does not contain carbon dioxide (at least not in appreciable quantities as a result of its electrolytic treatment) but may, on the other hand, contain gaseous chlorine in solution. In contrast, in the present process, the first electrolytic cell, which comprises a consumable anode of amorphous carbon, produces, as already mentioned, carbon oxidation products and particularly CO_2, which is recognised as necessary for the object envisaged. The second cell which preferably comprises a consumable anode of a ferrous

substance produces, as anodic reaction products, iron salts and oxides capable of fixing the free chlorine; in addition the free chlorine reacts with insoluble carbonates formed in the first cell to convert them into soluble chlorides.

The treated sea water which passes through the pipe 4 and which has acquired the properties indicated may be stored in a suitable receptacle instead of being taken direct to the consumer apparatus; it is then subsequently introduced into the latter, either intermittently or continuously.

In the course of the experiments we have carried out, the fixing of the free chlorine was found to be capable of preventing the acidity of the condensed water obtained in marine boilers. Experience has shown that if free chlorine is present in the steam produced, the condensed water which results is slightly acidified by chlorinated products such as HCl and HOCl.

Because of the presence of CO_2, the process described is likewise applicable to the treatment of partially softened non-chlorinated water containing lime or minerals.

Mention has also been made of the fact that the anodes of the two electrolytic cells I and II of the apparatus in Figures 1 and 2 are slowly destroyed by the anodic reactions which take place there; moreover, in a chlorinated liquid such as sea water, the cathodes may slowly become covered with a more or less adherent layer with a soda base to such an extent that these cells may lose their effectiveness after a certain time. In certain cases, however, it is important to maintain them in good order substantially without interupting the electrolytic treatment. For this purpose, said cells are constructed with a plurality of similar electrodes arranged side by side, at least one of which is not connected to the source of current and remains in reserve. This arrangement is illustrated in Figure 3 which shows a cell 20 comprising, on the one hand two similar anodes 21 and 21^1 and on the other hand, two similar cathodes 31 and 31^1, separated from the anodes by a porous diaphragm 30. Only the electrodes 21 and 31 are connected to the source of current while the electrodes 21^1 and 31^1 remain cut off. When the first are consumed or have deteriorated they are disconnected from said source while the second ones are connected thereto in turn. As can be seen from the figure, the positions of the various electrodes may be selected in such a manner that the length and shape of the lines of current in the electrolyte are substantially the same whichever set of electrodes is used. In this manner, the conditions of the electrolysis (density of current and quantities of products formed) are not affected by the change of electrodes which can be effected without interrupting operation.

In the arrangement shown in Figure 1, the two cells I and II are likewise upstream of the apparatus fed by the pipe 4. These cells are therefore both outside said apparatus. On the other hand, in the arrangement shown in Figure 2, one of the two cells, preferably the cell I, the anode of which is of amorphous carbon, is necessarily upstream of the other (since the liquid passes through them in series). It may therefore be advantageous, at least in certain cases, to arrange the cell II inside the apparatus to be fed and to which the pipes 10 and 12, provided with their respective valves, lead directly.

It will be understood that modifications may be made to the embodiments which have been described without going outside the scope of the present invention.

In particular, if the quantity of liquid to be treated is great, it is preferable to use a plurality of similar cells with anodes of amorphous carbon, connected and fed in parallel and a plurality of similar cells with metallic electrodes, likewise connected and fed in parallel and which, from the hydraulic point of view, may be associated in series with the former.

WHAT WE CLAIM IS:—

1. An electrolytic process for the treatment of sea water, brackish water or insufficiently softened water in order to reduce its tendency to form deposits of scale or other substances on the surfaces of apparatus such as boilers, evaporators, condensers and the like, and their pipes supplied with such water, which comprises passing the water to be treated through two diaphragm-type electrolytic cells, one of which includes at least one anode of amorphous carbon and the other at least one metallic anode, the cathodes of the two cells being metallic, discarding the cathodic effluents from the two cells, and using only their anodic effluents which are mixed in proportions such that the pH of the mixture is maintained within the range 4 to 6.4.

2. A process according to Claim 1, in which the pH of the mixed effluents is maintained at approximately 5.2.

3. A process according to Claim 1 or 2, in which the two electrolytic cells are supplied in parallel with the water to be treated, the anodic effluents of the two cells being mixed before their introduction into the apparatus supplied with the treated water.

4. A process according to Claim 1 or 2, in which the water to be treated is supplied to the cell having amorphous carbon anodes, the anodic effluent of this cell being supplied to the anodic compartment of the cell having metallic anodes, while untreated water is supplied to the cathodic compartment of the latter cell, only the anodic effluent of which is used to supply the apparatus supplied with the treated water.

5. A process according to any of the preceding claims, in which the electrolytic cells and the apparatus supplied with the treated water are supplied with their respective liquids through conduits provided with adjustable valves which enable the pH of the water supplied to said apparatus to be adjusted to said value.

6. A process according to any of Claims 1 to 3, in which automatic regulation means are provided to control the respective positions of the supply and output valves controlling the flow of liquid through the cells as a function of the measured pH value of the mixture of anodic effluents from the two cells.

7. A process according to Claim 4, in which automatic regulation means are provided to control the respective positions of the supply and output valves controlling the flow of liquid through the cells as a function of the measured pH value of the anodic effluent from the second cell, that is the cell comprising metallic anodes.

8. An electrolytic process for the treatment of sea water, brackish water or insufficiently softened water according to Claim 1 substantially as hereinbefore described.

9. An electrolytic process for the treatment of sea water, brackish water or insufficiently softened water in order to reduce its tendency to form scale deposits when carried out in apparatus substantially as hereinbefore described with reference to Figure 1, 2 or 3 of the accompanying drawing.

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Leamington Spa: Printed for Her Majesty's Stationery Office by the Courier Press.—1962.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

906440 COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of the Original on a reduced scale

Fig. 1

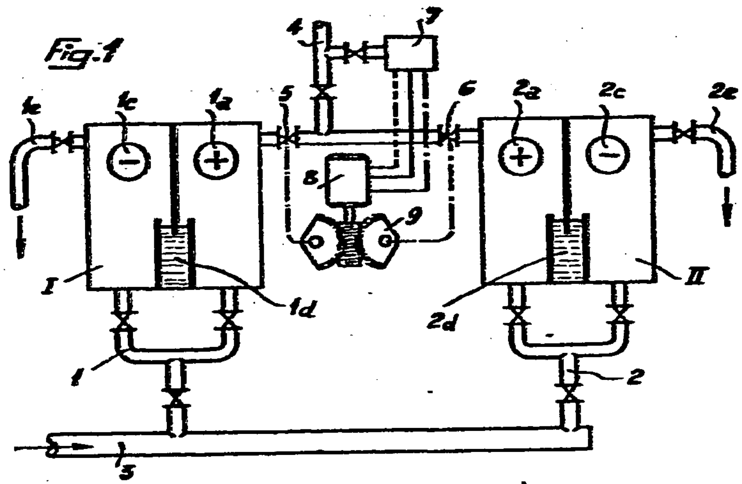

Fig. 2

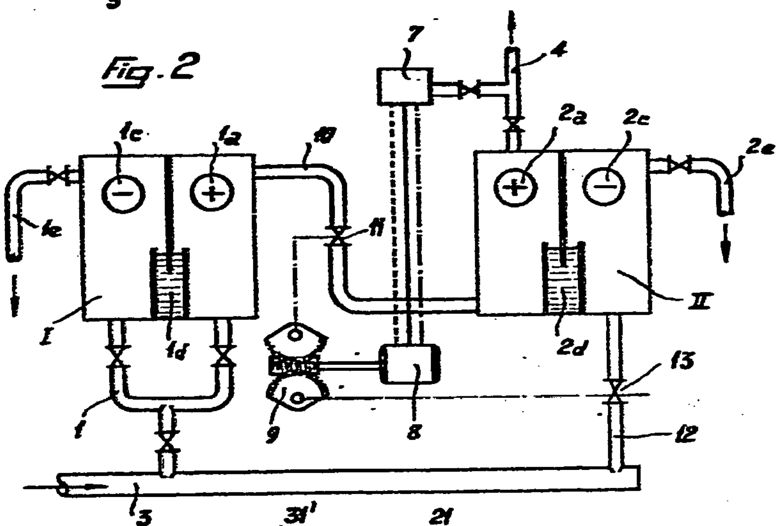

Fig. 3